REACTION OF IODINE AND SOME HETEROCYCLIC TERTIARY BASES WITH ACETONE AND METHYL ISOBUTYL KETONE*

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In an investigation of the reaction of compounds containing a reactive hydrogen atom, King[1] attempted to make some of the aryl methyl ketones react with iodine and pyridine. He was able to prepare substituted β-ketoalkylpyridinium iodides, accompanied by some hydroiodide of the base. This reaction was later extended to other bases,[2] namely α-, β-, γ-picolines, quinoline, isoquinoline, and 4-pentylpyridine. Krohnke[3] extended this work to acetone, reporting the isolation of acetonylene-bis(pyridinium iodide) and acetonylquinolinium iodide in poor yields. In all these reactions excess of the base formed the medium of reaction and no other solvent was used. We have now prepared three new compounds, *N*-acetonylpyridinium iodide, *N*-acetonyl-β-picolinium iodide, and *N*-(4-methyl-2-oxopentyl)quinolinium iodide by using methanol as medium for King's reaction. The yield of *N*-acetonylquinolinium iodide was also improved by this method. The preparation of phenacylpyridinium iodide as reported by King was also tried on these lines, and was found to give satisfactory results. The advantageous use of methanol in this reaction is that there are no side reactions, and the separation of quaternary β-ketoalkyl iodide from the corresponding hydroiodide of the base is facilitated, the latter being more soluble in methanol. The amount of the base used was also less.

Isoquinoline with acetone and iodine in methanol gave only its hydriodide, and no substituted β-ketoalkyl derivative could be isolated. α- and γ-Picolines failed to give any solid derivative even on using higher-boiling alcohols like benzyl and isopentyl alcohol as solvent. Methyl ethyl ketone failed to give any isolable product with these bases.

Experimental

All reagents were thoroughly dried and purified before use. All melting points were determined on a Kofler instrument; the compounds melt with decomposition. Yields were calculated with respect to ketone.

Procedure

Iodine (0·1 mole) was dissolved in 20 ml of the base. This solution was added to 0·1 mole of the appropriate ketone present in 150 ml of methanol. The periodide of the base separated

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[1] King, L. C., *J. Am. chem. Soc.*, 1944, **66**, 894.

[2] King, L. C., and McWhirter, M., *J. Am. chem. Soc.*, 1946, **68**, 717.

[3] Krohnke, F., *Chem. Ber.*, 1959, **92**, 22.

immediately.[4] The reaction mixture was heated under reflux on a water-bath for 2–10 hr, and then left overnight or even for a week in the case of quinoline. The crystals of the periodide of the base disappeared and fresh crystals of the β-ketoalkyl derivative were formed. These were filtered, washed with methanol, and then recrystallized from 50% methanol. The filtrate was concentrated and yielded the hydriodide of the base on cooling. Some trace of the β-ketoalkyl iodide was also present; it was separated through its differential solubility in methanol.

In an alternative method the reaction mixture of the base, iodine, and the ketone in methanol was kept for 2 weeks at room temperature. The periodide of the base slowly disappeared and the respective β-ketoalkyl iodide crystallized out; it was worked up in the usual way. The critical data of the various compounds obtained are given below.

Compounds

N-Acetonylpyridinium iodide.—Colourless needles, m.p. 230°, yield 30% (Found: I, 48·6; N, 5·4. $C_8H_{10}INO$ requires I, 48·2; N, 5·3%). *Picrate*, m.p. 205°. *Perchlorate*, m.p. 260° (Found: N, 5·8. Calc.: N, 5·9%).

N-Acetonylquinolinium iodide.—Yellow prisms, m.p. 212° (lit.[3] 207–209°), yield 50% (Found: I, 40·7; N, 4·5. Calc. for $C_{12}H_{12}INO$: I, 40·5; N, 4·5%). Picrate, m.p. 215–217°. Perchlorate, m.p. 189–190° (Found: N, 4·7. Calc.: N, 4·9%).

N-Acetonyl-β-picolinium iodide.—Colourless needles, m.p. 235°, yield 30% (Found: I, 45·3; N, 5·2. $C_9H_{12}INO$ requires I, 45·8; N, 5·1%). *Perchlorate*, m.p. 262° (Found: N, 5·4. Calc.: N, 5·6%).

N-(4-Methyl-2-oxopentyl)quinolinium iodide.—Yellow needles, m.p. 180–182°, yield 40% (Found: I, 41·8; N, 4·75. $C_{15}H_{18}INO$ requires I, 41·6; N, 4·7%). *Picrate*, m.p. 140°. *Perchlorate*, m.p. 145° (Found: N, 4·1. Calc.: N, 4·3%).

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[4] Saxena, J. P., and Gelra, M. R., unpublished data.